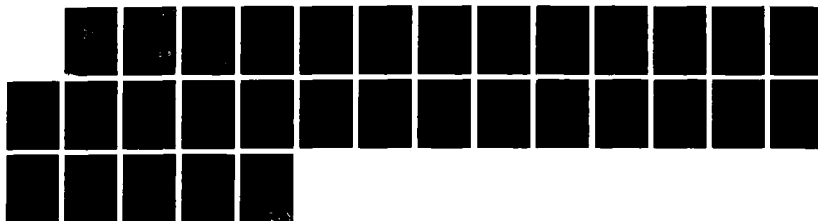
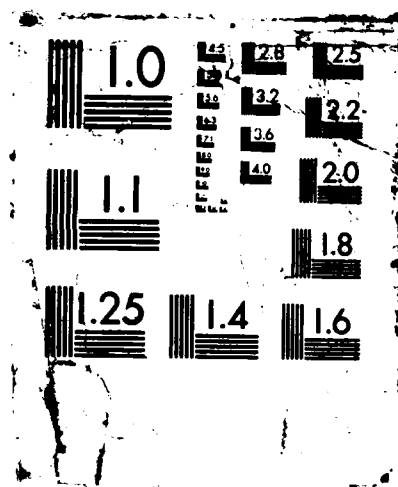


AD-A193 376 CHEMICAL AND PHOTOCHEMICAL REACTIVITY IN MICROEMULSIONS 1/1  
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UNCLASSIFIED DAJA45-85-C-0024 F/G 7/3 NL





R+D. 5037-CH-01 (2)

CHEMICAL AND PHOTOCHEMICAL REACTIVITY IN MICROEMULSIONS AND WATERLESS  
MICROEMULSIONS

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Pr. A.LATTES and Dr.M.T. MAURETTE  
Université Paul Sabatier de TOULOUSE

DAJA 45-85-C-0024

"First Periodic Report"

Date: November 1985 - December 1985

"The research reported in this document has been made possible through the support and sponsorship of the U.S. Army. This report is intended only for the internal management use of the contractor and the U.S. Government".

*Periodic Interim repts. 1-5,  
November 1, 1985 - January 31, 1988.*

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PART 1

WATERLESS MICROEMULSIONS - DIELS-ALDER REACTION OF CYCLOPENTADIENE AND METHYLACRYLATE AS A PROBE OF FORMAMIDE MICROEMULSIONS.

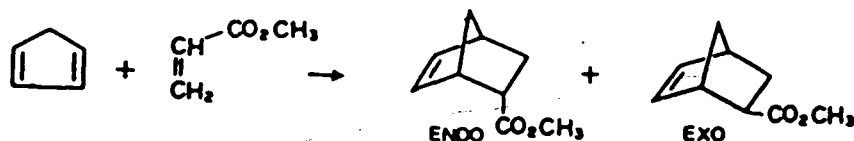
A. AHMAD-ZADEH SAMII, A. de SAVIGNAC, I. RICO and A. LATTES



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Recently, we have reported that it is possible to prepare microemulsions by replacing water with the highly structured solvent, formamide. Physicochemical studies of such media have been published.

We report here the first use of such non-aqueous microemulsions as reaction media. We carried out a Diels-Alder addition of methyl acrylate to cyclopentadiene in various formamide microemulsions. This type of reaction, which is highly sensitive to the polarity of the medium, can be used as a chemical probe of microemulsion.



#### Preparation of the reaction media : monophasic areas of formamide microemulsions

We replaced water with formamide, and we used a visual transparency criterion to determine the phase diagram . An ionic system was used with isooctane as oil, 1-butanol as cosurfactant and cetyltrimethylammonium bromide (CTAB) as surfactant. Figure 1 shows the pseudo ternary phase diagram for (formamide/CTAB = 2, 1-butanol, isooctane) mixtures.

We carried out a preliminary study of the influence of the various constituents of the microemulsion on the reaction.

#### Effect of microemulsion components on the probe reaction

Table I summarises the results obtained in different solvents.

Formamide, which strongly favours solvophobic interactions would seem, therefore, to be an excellent medium for Diels-Alder reactions, especially at high concentrations. By using formamide, we have obtained considerably improved stereoselectivities at high concentrations, over those obtained by BRESLOW in water (for C = 0.30 mole/l, ENDO/EXO = 5.3 for water, and 6.7 for formamide). It is interesting that contrary to the results in water, where the reaction takes place in a heterogeneous medium, concentration effects were not observed in formamide. The same stereoselectivity was obtained whatever the substrate concentration. This is probably due to the fact that in formamide the reaction takes place in a homogeneous medium.

In addition, the use of formamide as a homogeneous reaction medium significantly improves yield. For water, the yields of product (after extraction) do not exceed 40%, whereas in formamide, the yields are quantitative whatever the initial concentrations of the reactants. The yields of isolated product (after extraction) are then close to 85%.

#### Diels-Alder reactions in formamide microemulsions

As opposed to results obtained for the same type of reaction in aqueous microemulsions without cosurfactant (only studied in the continuous oil phase), we have been able to exploit the high solubility of substrates in formamide to investigate the complete microemulsion phase diagram (continuous oil phase and continuous formamide phase).

Representative points of the microemulsions studied are shown on figure 1.

The results demonstrated the presence of two zones in the microemulsions studied :

- a zone of relatively low selectivity in the oil rich part of the diagram
- a much wider zone of higher selectivity.

Good agreement between the changes in conductivity and endo/exo selectivity are found along the lines AF and FK (demixtion line) on a plot of these changes as a function of the formamide volumic fraction  $\phi$  (figures 2 and 3).

The abrupt changes in selectivity and conductivity around C on line AF, and around G on the demixtion line can be attributed to phase inversion from reverse micelles (formamide in oil) to direct micelles (oil in formamide).

#### Conductivity changes

This type of change in conductivity has been demonstrated, for aqueous microemulsions, to be due to percolation, in which there is a concatenation of reverse micelles of water in oil, followed almost immediately by a phase inversion from reverse (low conductivity zone) to direct micelles -(higher conductivity zone).

#### Selectivity change

##### Reverse micelles

In the continuous oil phase of microemulsions G, it appears that the

reaction takes place in the continuous phase. The endo/exo ration (= 2.85) is close to that obtained for pure isooctane (= 2.3 -Table I).

#### Direct micelles

On the other hand, in the formamide rich zone, the endo/exo ration (= 4.5) obtained in microemulsion K is virtually the same as that found in the alcohol rich microemulsion A. This value is also close to that found in pure butanol (= 5.0 - table I). It would seem that the reaction takes place at the micelle interface in the continuous formamide phase.

### CONCLUSION

This Diels-Alder reaction is a valuable probe reaction for the study of formamide microemulsions. It is able to discriminate the continuous oil phase from the continuous structured phase (formamide or alcohol rich).

#### RESEARCH PATTERN

- Supplementing the physical chemical study of the microemulsion medium involving ionic surfactants with density measurements.
- Studying the reactivity in microemulsion medium involving non ionic polymeric surfactants.

#### REFERENCE

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Table 1 ENDO/EXO product ratios in organic media and in water.

Solvent	Dielectric constant $\epsilon$ (20-25°C)	Concentration of diene and dienophile (M)	ENDO/EXO <sup>a</sup>
Isooctane	2.0	0.15	2.3
1-butanol	17.1	0.15	5.0
Water	78.5	0.15	7.4 (9.2 <sup>b</sup> )
Water	78.5	0.30	5.3 (5.9 <sup>b</sup> )
Formamide	109.0	0.07	6.9
Formamide	109.0	0.15	6.7
Formamide	109.0	0.30	6.7

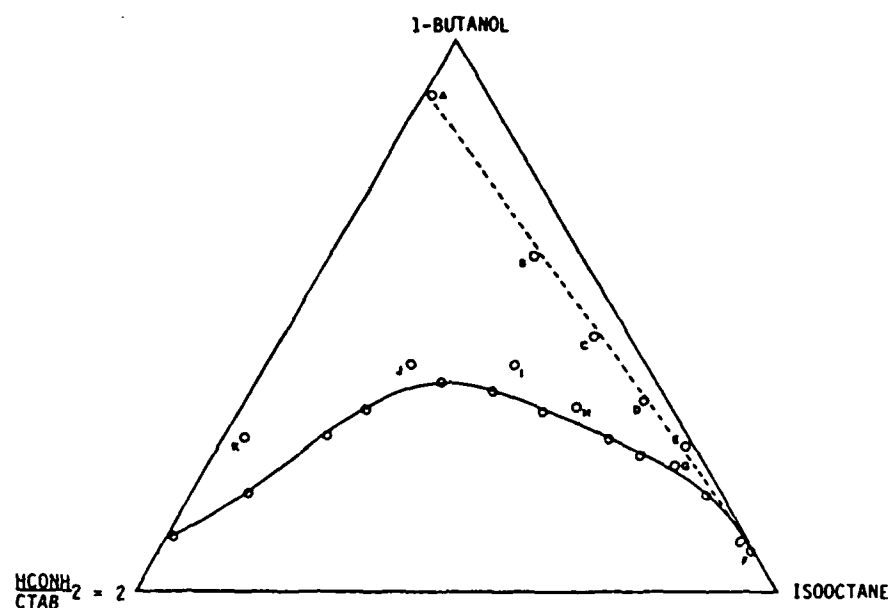


Figure 1 : Pseudo ternary phase diagram of the system-formamide/CTAB = 2, 1-butanol, isooctane.

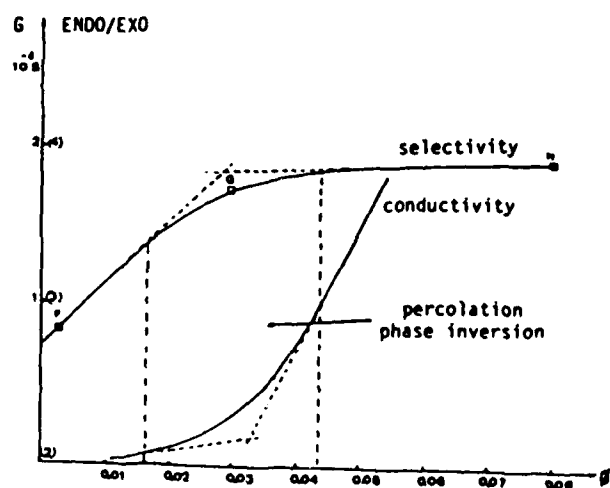


Figure 2

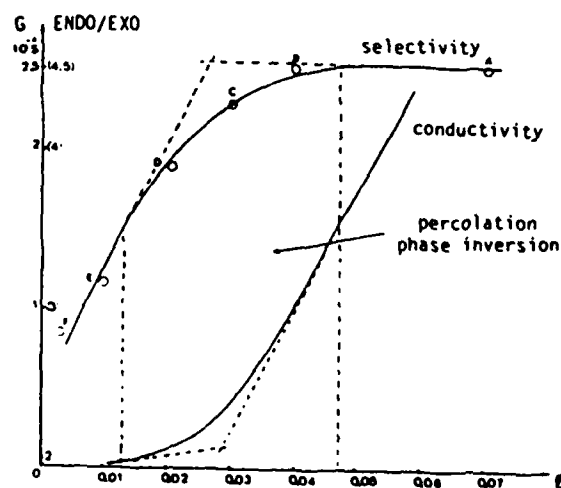


Figure 3

Figure 2 : Plot of conductivity and endo/exo ratios as a function of the formamide volumic fraction  $\phi$ , along the demixion line.

Figure 3 : Plot of conductivity and endo/exo ratios as a function of the formamide volumic fraction  $\phi$ , along the demixion line.



## OXIDATIONS BY HYDROPEROXIDES IN MICROEMULSIONS.

E. OLIVEROS and M.T. MAURETTE

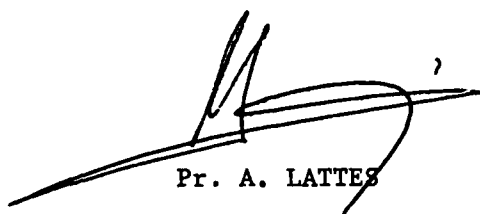
- ◆ Microemulsions based on benzyldiméthyltétradecylammonium chloride and sodium dodecylsulfate (for comparison) and containing 30% hydroperoxide instead of water have been prepared. Ammonium bromides cannot be used as surfactants because they are instantaneously oxidized by  $H_2O_2$ . Butanol-1 and tert-butanol have been used as cosurfactants. Phase diagrams are not dramatically modified by addition of hydrogen peroxide to the microemulsions.
- ◆ Two methods of titration of the hydrogen peroxide in the microemulsions have been tested on freshly prepared microemulsions containing a know amount of hydrogen peroxide:
  - titration with potassium permanganate; despite the fact that potassium permanganate reacts very slowly at room temperature with butanol-1, and that the microemulsion breaks into two phases, hydrogen peroxide can be reproducibly titrated by this method up to a concentration of 5% in the medium (blank experiments are made with microemulsions without hydrogen peroxide);
  - density measurements: in a first step we have verified that density measurements on aqueous solutions of hydrogen peroxide at different concentrations follow a linear correlation (ideal mixture). Measurements in microemulsions are in progress in order to evaluate the rate of decomposition of  $H_2O_2$ .
- ◆ The first reaction tested in an anionic and a cationic "oil in water" microemulsion is the oxidation of the 1,3-dihydroxynaphtalene by  $H_2O_2$  under alkaline conditions. The first step of the reaction, i.e. the formation of the 2-hydroxy-1,4-naphtoquinone (lawsone), is very fast in the two microemulsions as well as in aqueous solution. However, further oxidation, that is oxidative ring opening and subsequent formation of the corresponding dicarboxylic acid, is slower and its rate depends strongly on the environment: it seems that the deprotonated lawsone is stabilized as a counterion of the positively charged aggregate and thus formation of the 1,2-quinoid intermediate, necessary for further oxidation, is much slower.

Experiments with others hydroxynaphtalene in various microemulsions "water in oil" and "oil in water" will follow.

Financial statement

As of December 31, US \$ 6535 have been paid in salaries leaving an amount of unused funds of US \$ 15250.

TOULOUSE, December 27, 1985



Pr. A. LATTES



Dr. M.T. MAURETTE

CHEMICAL AND PHOTOCHEMICAL REACTIVITY IN MICROEMULSIONS AND WATERLESS  
MICROEMULSIONS

Pr. A. LATTES and Dr. M.T. MAURETTE  
Université Paul Sabatier de TOULOUSE

DAJA 45.85.C.0024

"Second Periodic Report"

Date: January 1986 - May 1986

"The research reported in this document has been made possible through the support and sponsorship of the U.S. Army. This report is intended only for the internal management use of the contractor and the U.S. Government".

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PART 1

WATERLESS MICROEMULSIONS AS REACTION MEDIA

I. RICO, A. de SAVIGNAC and A. LATTES

## WATERLESS MICROEMULSIONS AS REACTION MEDIA

### I - Diels-Alder reactions in formamide microemulsions

#### a) Overview

In the previous report, we indicated that the Diels-Alder reaction could be used as a chemical probe for analysis of the structure of a microemulsion. The break in the curve of the plot of reaction selectivity against microemulsion composition in the oil rich zone was attributed to percolation or phase inversion (1).

#### b) New results

A structural analysis of microemulsions has been carried out using diffusion of RX of small angles (in collaboration with Prof. C. Petit Pas, Rouen) (2).

The results show clearly that, in the oil rich zone, the aggregates are filamentous and not spherical as found in aqueous systems. This study also showed that these aggregates percolate, producing large interfaces in the zones where we observed breaks in slope in reaction specificity and electrical conductivity.

The results are generally coherent and suggest that the Diels-Alder reaction can be used as a probe reaction for investigation of formamide microemulsions.

We are continuing these investigations in formamide microemulsions prepared with nonionic surfactants (3).

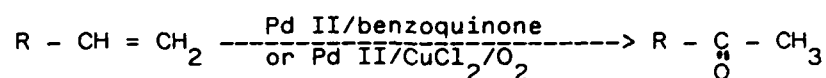
Moreover, in line with the priorities drawn up in the original project, we are investigating:

- a) solubilization of various compounds
- b) nucleophilic displacement and oxidation reactions.

An investigation of the Wacker process ( oxidation of olefins catalyzed by palladium salts) in formamide microemulsions has been started.

## II - Wacker process in formamide microemulsions

The reaction can be outlined as follows:



The most common commercially available palladium II salt is  $\text{PdCl}_2$ , which unfortunately is virtually insoluble in most organic solvents and water (0.7 g/l). In order to be used it must be converted to soluble palladium (II) species such as  $\text{PdCl}_2(\text{PhCN})_2$  or  $\text{PdCl}_2(\text{MeCN})_2$ .

However, it is sufficiently soluble in formamide (50 g/l) to be used directly. In order to obtain homogeneous mixtures of olefin and formamide we prepared formamide microemulsions of composition  $\text{R}-\text{CH}=\text{CH}_2$  with  $\text{R} = \text{C}_4\text{H}_9$  or  $\text{C}_{10}\text{H}_{21}$ , pluronic<sup>L</sup> 64 as surfactant, and isopropanol as cosurfactant. Native  $\text{PdCl}_2$  can be employed in this medium.

The yields of ketone are a function of the composition of the microemulsion. We are in the process of optimizing these conditons. Yields obtained at present are higher than those obtained using classical methods (> 50%).

In addition, having previously studied the structure of waterless microemulsions based on fluorinated olefins (3,4) we have commenced a

similar study in this type of medium.

The preliminary results on oxidation reactions will be described in the next report.

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PART 2

OXIDATIONS BY HYDROPEROXIDES IN MICROEMULSIONS

E. OLIVEROS and M. T. MAURETTE

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During the past four month, the financial support from ERO has been used to developped the part 1 of the contract DAJA 45.85.C.0024: "Waterless microemulsions as reaction media" (Professor Lattes's group). We had thus no means to persue our project other than for some qualitative experiments in views of the collaboration with the group of Dr.Braun in Lausanne.

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Financial statement


As of May 31, US \$ 17428 have been paid in salaries leaving an amount of unused funds of US \$ 4357.

TOULOUSE, May 27, 1986

Pr. A. LATTES

A stylized handwritten signature consisting of several overlapping loops and a long horizontal stroke extending to the right.

Dr. M.T. MAURETTE

A handwritten signature that includes the word "Maurette" in a cursive script, preceded by a large loop and a vertical line.

CHEMICAL AND PHOTOCHEMICAL REACTIVITY IN MICROEMULSIONS AND WATERLESS  
MICROEMULSIONS

Pr. A. LATTES and Dr. M.T. MAURETTE  
Université Paul Sabatier de TOULOUSE

DAJA 45.85.C.0024

"Third Interim Report"

Date: June 1986 - January 1987

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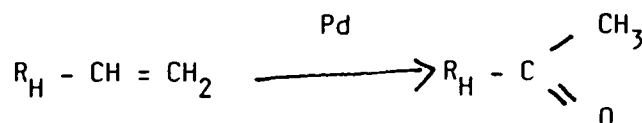
## Part I - Waterless microemulsions as reaction media

I. RICO, A. de SAVIGNAC, A. LATTES


The study of Diels-Alder reactions as chemical probes for analysis of the structure of formamide microemulsions is now finished, bothly with ionic and non-ionic surfactants (1,2).

The use of such probes showed different kinds of aggregates which have been corroborated by XR scattering (3).


We are now investigated oxidation reactions and nucleophilic displacements in these waterless media.

1 - Oxidation reactions : transformation of olefins1.1. - conversion of hydrogenated olefins in ketones by the wacker process

The most common commercially available and the cheapest Palladium <sup>II</sup> salt is PdCl<sub>2</sub>, which is unfortunately insoluble in most organic solvents and in Water. However it is highly soluble in formamide and so it can be used in microemulsions.

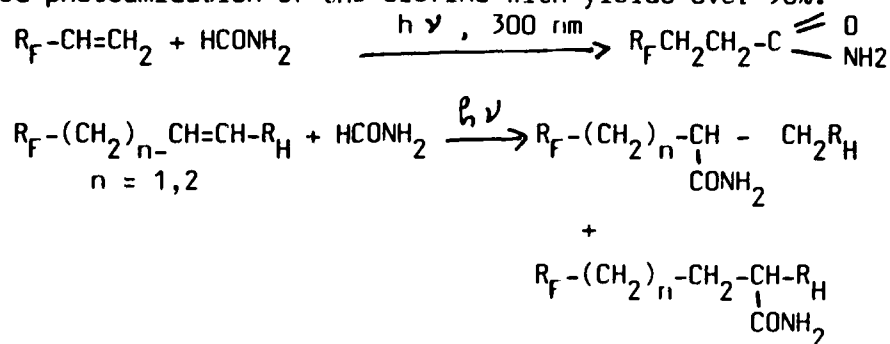
By optimization of the formamide microemulsion with C<sub>9</sub>H<sub>19</sub>--(OCH<sub>2</sub>CH<sub>2</sub>)<sub>8</sub>-OH as surfactant and propanol-2 as cosurfactant, we have been able to oxidize hexene-1 to hexanone-2 with yields over 90% and very short times of reaction, shorter than in classical media. Moreover, it is possible to realize the reaction continuously by progressive addition of hexene-1 to the microemulsion. The turn-over is over 10 000 (4). We are now studying the mechanism of this reaction in microemulsions, to pitimize it with various olefins.

1.2. - Photoamidation of fluorinated olefins

In formamide microemulsions, based on fluorinated olefins (5,6) (R<sub>F</sub>-CH=CH<sub>2</sub> , R<sub>F</sub>(CH<sub>2</sub>)<sub>n</sub> - CH=CH-R<sub>H</sub> ; n = 1,2 ) we have not been able to realize the wacker process. The fluorinated olefins are not sufficiently reactive. However, by irradiation of these transparent microemulsions (optimized with C<sub>9</sub>H<sub>19</sub> --(OCH<sub>2</sub>CH<sub>2</sub>)<sub>n</sub>-OH as surfactants and C<sub>4</sub>F<sub>9</sub>C<sub>2</sub>H<sub>4</sub>OH as cosurfactant),

n = 4 ... 12

we obtained photoamidation of the olefins with yields over 90%.

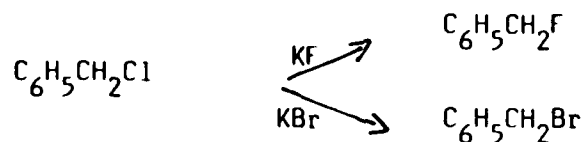


The final amides are now used by ATOCHEM in the composition of fire extinguishers (7).

For  $R_F-(CH_2)_n-CH=CH-R_H$ , we are now trying to correlate the structure of microemulsions to the regioselectivities of the reaction.

## 2 - Nucleophilic displacements

In a preliminary study, we choose the bromation (and fluoration) of  $C_6H_5CH_2Cl$ , which has been recently studied in aqueous microemulsions (8) :



We used microemulsions constituted by formamide, isooctane, CTAB as surfactant and 1-butanol as co surfactant. These microemulsions are now well known in our group (1,3).

Firstly, we compared the fluoration and the bromation of  $RCI(C_8H_{17}Cl$  and  $C_6H_5CH_2Cl$ ) in phase - transfer conditions to compare the effect of water and formamide. With formamide in place of water, we found that by-products obtained <sup>in</sup> water (e.g. ROH, ROR) are eliminated leading to better yields in RX (X = Br, F) (9).

We are now studying these reactions in formamide microemulsions from a kinetic point of view.

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## PART 2

### OXIDATIONS BY HYDROPEROXIDES IN MICROEMULSIONS

E. OLIVEROS and M.T. MAURETTE

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During the past six months, the financial support from ERO has been used to develop the part 1 of the contract DAJA 45-85-C-0024: "Waterless micro-emulsions as reaction media" (Pr. Lattes's group). However we made some experiments on our project in the context of our collaboration with the group of Dr. Braun in Lausanne.

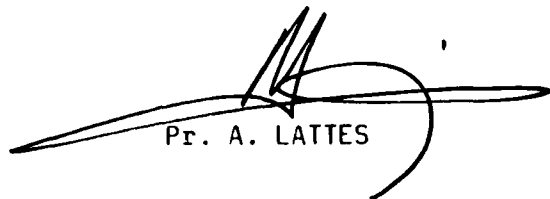
In the project of developping four components perfluorinated microemulsions, we try to formulate systems with tri-n-butylamine as a cosurfactant. The choice of this product has been suggested due to the industrial availability of its perfluorinated homologs. So far, no transparent and fluid Winsor IV region has been detected in phase diagrams of sodium laurate, tri-n-butylamine, cyclohexane, water.

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Financial statement

As of february 15, US \$ 27785 have been paid in salaries leaving an amount of unused funds of US \$ 14000 .

TOULOUSE, February 9, 1987



Pr. A. LATTES



Dr. M.T. MAURETTE

CHEMICAL AND PHOTOCHEMICAL REACTIVITY IN MICROEMULSIONS AND WATERLESS  
MICROEMULSIONS

Pr. A. LATTES and Dr. M.T. MAURETTE  
Université Paul Sabatier de TOULOUSE

DAJA 45-85-C-0024

"Fourth Interim Report"

Date: february 1987 - July 1987

"The research reported in this document has been made possible through the support and sponsorship of the U.S. Army. This report is intended only for internal management use of the contractor and the U.S. Gouvernement."

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## Part I - Waterless microemulsions as reaction media

I. RICO, A. de SAVIGNAC, A. LATTES

The last part of our work concerning the study of Diels-Alder reactions as chemical probes for analyzing the structure of non aqueous microemulsions has been published (1). Three reviews, summarizing our first observations in such media have been edited as 3 chapters in two books (2,3,4).

We have determined the structure of aggregates in formamide and developed new oxidation reactions on transformation of olefins.

STRUCTURE OF AGGREGATES IN FORMAMIDE

Contradictory results have been reported on the production of micelles in formamide using ionic surfactants. We demonstrated molecular aggregation in formamide, but only above the Krafft temperature, which itself depends on the nature of the surfactant and the medium. Cmc were determined from surface tension measurements for CTAB and SDS at 60°C in formamide. The cmc were considerably higher in formamide than in water, and the corresponding Krafft temperature for these surfactants were also higher in formamide than in water. These results can be explained by the structure of formamide, which can be considered as a low-melting anhydrous fused salt (5). It is the end of a challenge.

To corroborate the existence of micelles, the phase diagram of CTAB in formamide was determined. Two mesomorphic phases (an hexagonal and a lamellar) were observed, which closely resembled these found in water/CTAB system. Furthermore, the micellisation of CTAB in formamide was visualised and studied by  $^1\text{H}$  NMR (6).

These results demonstrate than formamide can substitute for water in systems involving molecular aggregation.

OXIDATION REACTIONS: TRANSFORMATION OF OLEFINS

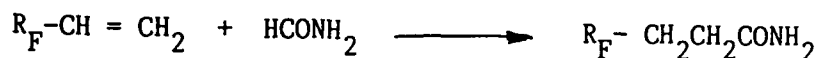
## 1) Investigation of the Wacker Process in formamide microemulsions

The preliminary study of this work has been submitted for publication and is in press (7). The reaction can be take place with olefins difficult to oxidize: internal olefins and styrene. The reaction kinetics were studied: in microemulsions the main feature was the absence of an induction period and an increase in overall reaction rate, demonstrating the existence of an autocatalytic process.

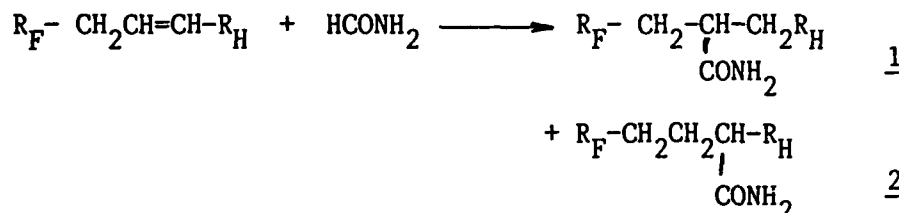
This approach shows considerable promise in homogeneous catalytic processes (oxidation, substitution, etc...).

## 2) Photoamidation of fluorinated olefins

In the last report we discussed the amidation of olefins:



We have finished the amidation of mixed olefins:



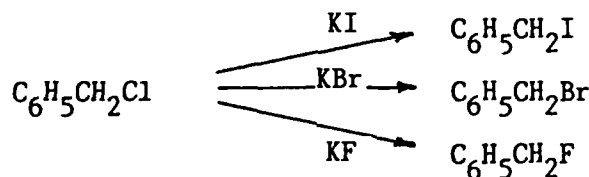
and correlated the structure of microemulsions to the regioselectivities of the reaction.

The segregation of perfluorinated and hydrogenated moieties oblige the  $R_F$  chain to be at the interface and we have been able to obtain selectively amides 1 or 2 with high yields.

The hydrolysis of amides in acids has been patented (8).

### Nucleophilic displacements

The kinetic studies of nucleophilic displacement:



in formamide microemulsions, shows that this type of process is not competitive is not competitive to the phase-transfer conditions.

The phase diagram of different microemulsions is explored to correlate the reactivity to the structure and eventually optimize the process.

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## Part II - OXIDATIONS BY HYDROPEROXIDES IN MICROEMULSIONS

E. OLIVEROS and M.T. MAURETTE

During the past six months, the financial support from ERO has been used to develop the part I (Pr. Lattes's group) of the contract DAJA 45-85-C-0024. Nevertheless, we made some experiments on our project: part II. Several microemulsions have been prepared with sodium dodecyl sulfate and benzyldimethyltetradecylammonium chlorid as surfactants, butanol-1 as cosurfactant water and cyclohexane:

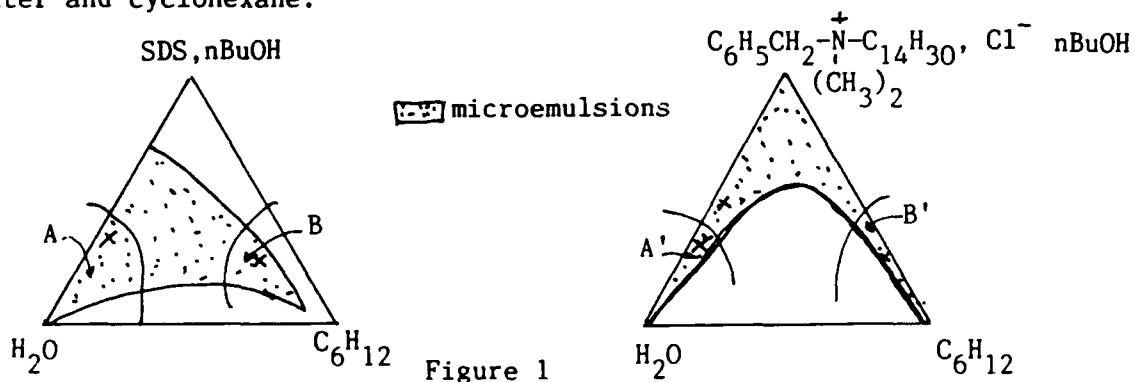


Figure 1

The source of H<sub>2</sub>O<sub>2</sub> is the sodium perborate added to the different microemulsions. Two kinds of reactions have been studied, the oxidation of phenylsulfide and the oxidation of 1,3- and 1,5-dihydroxynaphtalene

The most important difference between sodium perborate and microemulsions containing H<sub>2</sub>O<sub>2</sub> is that the former does not need basic pH. Otherwise, the reactions are faster with ammonium salt, particularly in the regions A and A' (figure 1).

#### 1) Sodium perborate and phenylsulfide

Neither phenylsufone nor phenylsulfoxide are produce by oxidation. The structure of the synthetised compound is studiing by mass spectra, UV, IR and NMR.

#### 2) Sodium perborate and naphtalenediols-1,3 and -1,5

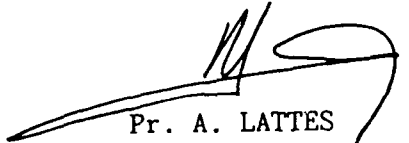
As with H<sub>2</sub>O<sub>2</sub>, lawsone (2-hydroxy-1,4-naphtoquinone) is obtained when we add sodium perborate to the microemulsions containing 1,3-dihydroxynaphtalene. We observed a total decomposition of 1,5-dihydroxynaphtalene unlike with H<sub>2</sub>O<sub>2</sub>.

The kinetics studies with the whole reactions (H<sub>2</sub>O<sub>2</sub> and sodium perborate) are actually in progress.

Financial statement

As of July 30, US \$ 37,785 have been paid in salaries leaving an amount of unused funds of US \$ 4000.

TOULOUSE July 20, 1987



Pr. A. LATTES



Dr. M.T. MAURETTE

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CHEMICAL AND PHOTOCHEMICAL REACTIVITY IN MICROEMULSIONS AND WATERLESS  
MICROEMULSIONS

Pr. A. LATTES and Dr. M.T. MAURETTE  
Université Paul Sabatier de TOULOUSE

DAJA 45.85.C.0024

"Fifth Periodic Report"

Date: July 1987 - January 1988

"The research reported in this document has been made possible through the support and sponsorship of the U.S. Army. This report is intended only for the internal management use of the contractor and the U.S. Government".

*Coquette A*

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CONTRAT NR-DAJA 45-85-L.0024

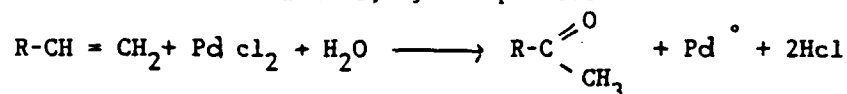
## Part I - Waterless microemulsions as reaction media

I. RICO, A. de SAVIGNAC, A. LATTES

During the last six months, the following objectives have been developed :

1- Investigation of the wacker process in formamide microemulsions: oxidation of olefines in ketones.

The first part of our work was to oxidize terminal olefines in ketones, in formamide microemulsions, by the process :



$\text{PdCl}^{\text{II}}$  was regenerated by benzoquinone



In order to obtain homogeneous systems, we used microemulsions consisted of formamide (and water), olefines as oils, propan-2-ol as cosurfactant and  $\text{C}_9\text{H}_{19} \begin{array}{c} \text{---} \text{C}_6\text{H}_4 \text{---} \end{array} (\text{OCH}_2\text{CH}_2)_8\text{OH}$  as surfactant. A typical phase diagram is given in figure 1.

The reaction kinetics obtained in microemulsions M and N,  $\text{HCONH}_2 \cdot \text{H}_2\text{O}$  and in  $\text{DMF} \cdot \text{H}_2\text{O}$  (classical medium) are shown in figure 2 :

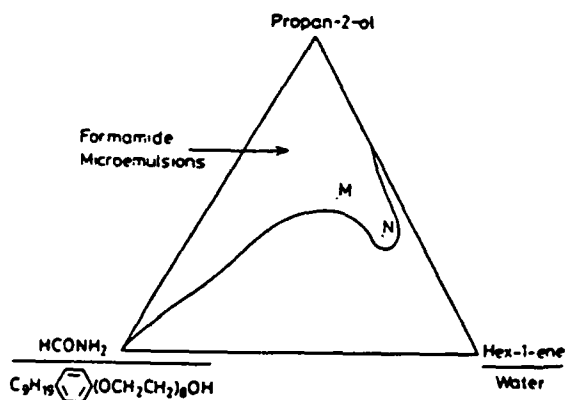


Figure 1. Phase diagram of the Wacker catalytic microemulsion system  $\text{HCONH}_2 \cdot \text{C}_9\text{H}_{19} \begin{array}{c} \text{---} \text{C}_6\text{H}_4 \text{---} \end{array} (\text{OCH}_2\text{CH}_2)_8\text{OH}$  (2:1 w/w)-propan-2-ol-hex-1-ene-water (1.56:1 w/w).

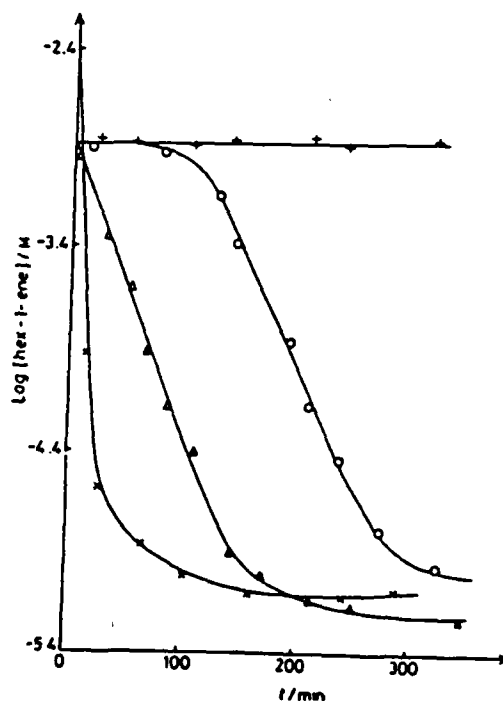
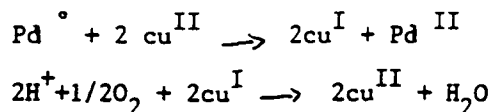


Figure 2. Kinetics of Wacker oxidation of hex-1-ene in  $\text{DMF} \cdot \text{H}_2\text{O}$  (O),  $\text{HCONH}_2 \cdot \text{H}_2\text{O}$  (+), and microemulsions M ( $\Delta$ ) and N ( $\times$ )

In the microemulsions (M and N), the main feature was the absence of an induction period. In such homogeneous media there is good contact between reactants and catalyst and the reaction starts immediately. More over the overall reaction was very much faster than in the water-DMF mixture until three-fold increase in reaction velocity (1). We have been able to oxidize similarly various olefines : hex-1-ene, oct-1-ene, dec-1-ene, dodec-1-ene, styrene, internal olefines (cis and trans) like pent-2-ene or hept-2-ene, for which regioselectivity studies are now in progress.

More over we have been able to realize these processes continuously with turn-overs over 10 000 (2)

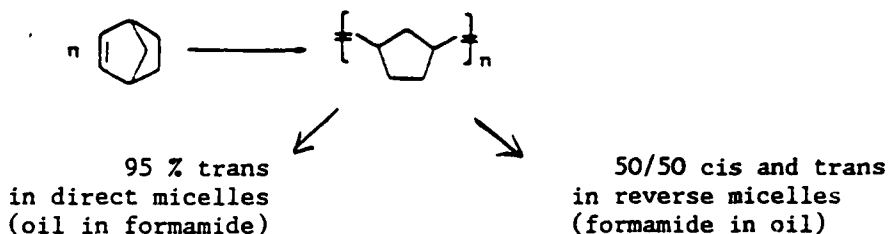
To ameliorate our process, we are now looking for formamide microemulsions working with  $\text{CuCl}_2/\text{O}_2$  instead of benzoquinone :



This approach shows considerable promise in homogeneous catalytic processes ; so, in a second part, we study also polymerization of olefines via metathetic reaction.

## 2 - Polymerization of norbornene, catalysed by $\text{RuCl}_3, 3\text{H}_2\text{O}$ in formamide microemulsions (3)

With the same catalyst ( $\text{RuCl}_3, 3\text{H}_2\text{O}$ ), by using formamide microemulsions (sodium dodecylsulphate as surfactant, butan-1-ol as cosurfactant, formamide and norbonene as oil) we have been able for the first time to strongly modify the stereochemistry of the following reaction :



The study of the mechanism is now in progress (4)

## REFERENCES

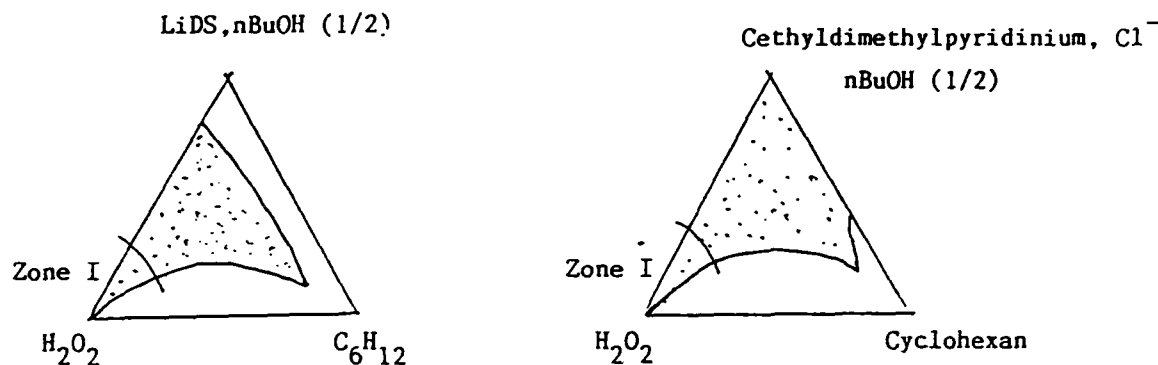
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"Formamide, a water substitute in microemulsions : use of a Diels-Alder reaction as a chemical probe". A. AHMADZADEH SAMII (1/02/1988)

## Part II - OXYDATIONS BY HYDROPEROXIDES IN MICROEMULSIONS

E. OLIVEROS and M.T. MAURETTE

During the past six months, the financial support from ERO has been used to develop the part I (Pr. LATTES's group).

We prepared several microemulsions with cetyltrimethylpyridinium chloride (A) or Li dodecylsulfate (B) as surfactants, butanol-1 and tertibutanol as cosurfactants, water or  $H_2O_2$  and cyclohexane:



 microemulsions

The phase diagrams are not very different when we used  $H_2O$  instead of  $H_2O_2$  so it is easier to compare the reactivity between  $H_2O_2$  and perborate. We can use almost the same microemulsion (zone I).

1) Microemulsions with  $H_2O_2$  or perborate and 1,3 naphthalenediol  
We obtained in all cases the formation of lawsone (as intermediate) but the reactivity is faster when perborate is used as source of  $H_2O_2$  and when the surfactant is the compound A (10 mn instead of 5 hours with microemulsion containing  $H_2O_2$ ).

### 2) Reactivity of phenylhydrazine

The formation of the compound is followed by UV spectroscopy. The reaction is very slow, but we observed an acceleration with microheterogeneous systems.

### 3) Oxidation of 1,4-naphthoquinone

In parallel with Pr. Braun's group, we studied the oxidation 1,4-naphthoquinone in microemulsions with Sodiumdodecylsulfate as surfactant and  $H_2O_2$ , at pH 7.4. We followed the reaction by UV spectroscopy and we observed the same acceleration: two times compared with homogeneous system.

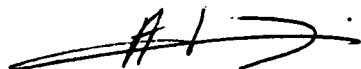
The kinetics studies with the whole reactions ( $H_2O_2$  and sodium perborate) are actually in progress.



Financial statement

As of February 15, US \$ 49,024 have been paid in salaries leaving an amount of unused funds of US \$ 16,891.

TOULOUSE February 10, 1988



Pr. A. LATTES



Dr. M.T. MAURETTE

END